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Thermochemical investigations of the methanol-isopropanol system

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THERMOCHEMICAL INVESTIGATIONS OF THE METHANOL-ISOPROPANOL SYSTEM

BY

ELMER LEE TAYLOR, 1937

A

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This Thesis is dedicated to my Mother,

Jewell Taylor,

born January 6, 1914.

ABSTRACT

Heats of solution and partial molar excess volumes at infinite dilution were determined for n-butanol, acetone, chloroform, and water in pure methanol, pure isopropanol, and several mixtures of the two at 25.0°C. The partial molar excess enthalpies of methanol and isopropanol were also determined and were combined to obtain integral heats of mixing.

All heat data were obtained using a calorimeter of the heat-leak design, containing approximately 300 ml of solvent. Sample sizes ranged from 0.1 to 8 ml. Individual heat measurements were reproducible to 0.05 calories and reported values are considered to be accurate to 1% + 0.5 calorie per mole.

Dilatometers of approximately 50 ml capacity were used for volumetric measurements. Sample sizes ranged from 0.1 to 1 ml. The volumetric measurements are considered to be accurate to 1% + 0.02 ml.

The heat of mixing of methanol - isopropanol is exothermic with a minimum of -19.0 calories per mole at 0.6 mole fraction isopropanol. All heats of solution and partial molar volumes showed negative deviations from the mole fraction average of the values obtained in the pure solvents. Heats of solution were combined with excess volumes to obtain values for E_v as a function of solvent composition.

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TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

LIST OF FIGURES

LIST OF TABLES

I. Introduction

Binary solvent systems have been of considerable interest to physical and physical organic chemists for many years. The ability to affect rate constants or the position of chemical equilibria with changes in the solvent composition appears to be an excellent tool for gaining insight into the molecular interactions which are involved in solvation. The usefulness of thermochemical data in the explanation of kinetic solvent effects has been demonstrated in the water-ethanol system[1]. While the measurement of heats of solution in binary solvent systems provides some answers to the kinetic solvent effect, a new problem arises, the explanation of the variation of the heat of solution with solvent composition.

Some explanations have been advanced for the variation in the heats of solution in terms of the effects on the "structure" of the solvent by the presence of the solute. In the water-ethanol system the explanation appears to have a strong basis. The fact that all the solutes that have been studied in the water-ethanol system show endothermic maxima in their heats of solution in the same general region of solvent composition indicates that "destructuring" has a large effect on the observed heats of solution. This effect is probably related in some way to the partial molar heats of water and ethanol [2,3].

These explanations appear to be qualitatively correct; however, the "solvent-solvent" interactions do not account for the variation in positions and shapes of the endothermic maxima for different

solutes. These variations must be due to some property of the solute; such as the number of solvent molecules affected, size, preferential solvation, ionization effects, or any combination of these and other effects.

It is apparent that with all the possible contributions to the solvent effect, explanation becomes nearly impossible. However, by a suitable choice of the solvent system some of the possible contributions to the solvent effect may be minimized. The choice of non-ionic solutes removes any problems due to the dielectric constant of the solvent.

The methanol-isopropanol solvent system was chosen for this investigation. Since the solvent components have similar structures, any effects due to structuring or destructuring of the solvent should be minimized. Also the components of the system have similar chemical properties, and the solvent system should exhibit fairly random solvation. The components of the system were chosen also for their variation in size. The solutes chosen for this investigation are all non-electrolytes to avoid any problems due to ionization. They cover a wide range of molecular sizes and chemical properties.

In this investigation the heats of solution of four solutes were determined in methanol-isopropanol mixtures as well as in the pure components. The apparent partial molar excess volumes of the same four solutes were also determined in the solvent system. In the course of this work it was convenient to determine quantities that closely approximate the differential heats of solution and

from these quantities the relative partial molar heats of solution of methanol-isopropanol were determined. The relative partial molar heats of solution were utilized to calculate the heat of mixing of the methanol-isopropanol system.

II. Literature Review

Heats of solution of an infinitely dilute third component in a mixed solvent system have not been investigated extensively. Systems that have been chosen for investigation have generally contained water as one component of the system.

C. M. Slansky[4] in 1940 determined the heat of solution at infinite dilution of electrolytes consisting of some of the alkali metal chlorides, bromides, and iodides at various solvent compositions in the water-methanol system. He observed that these salts all exhibited endothermic maxima in their heats of solution at a solvent composition of about 85 mole per cent water. He did not propose an explanation for the maxima. Arnett and his group[1] have reported data obtained in the water-ethanol system for a number of electrolytes and non-electrolytes. The solutes cover a wide range of sizes. Their results for electrolytes show behavior similar to that reported by Slansky. Arnett found that on comparing electrolytes with nonelectrolytes of very nearly the same size, the heats of solution of the electrolytes exhibited a smaller endothermic maximum than did the nonelectrolytes. Arnett has proposed an explanation for the maxima in the heats of solution in terms of structural effects on the solvent. This explanation is based on Franks and Ives'[5] evaluation of the literature on aqueous alcohol solutions. They found that the addition of the first increments of a low molecular weight alcohol and possibly other solvents to water causes an increase in the degree of structure. The heats of

solution of alcohols go through endothermic maxima in the region containing primarily water.

Bertrand et al.[2] have reported measurements in the water-ethanol and water-methanol solvent systems. They have shown by the results of calculations of the excess partial molar entropy that the addition of either component to the other pure component has a structure-forming influence in the water-ethanol system. The solutes studied in these two systems are exclusively electrolytes. Their reported results on the heats of solution of electrolytes are in general agreement with those of Arnett and Slansky.

Bertrand, Larson, and Hepler[3] have also reported data on the heats of solution at infinite dilution of several solutes in the water-triethylamine system. They have shown by calculations of the excess partial molar entropies that triethylamine increases the amount of structuring in dilute aqueous solutions. They have measured the heats of solution of ethanol, n-propanol, the four isomers of butanol, benzene, and chloroform. The solutes give results that are similar to the results in the water-ethanol system. The heats of solution of these solutes go through a maxima at a solvent composition greater than 70 mole per cent water. The heights of the maxima are greater for large solute molecules than for small solute molecules as was observed for the water-ethanol system.

Ben-Naim and Baer[6] have measured the solubility of argon in water-ethanol solvent system as a function of temperature. From their data they were able to calculate the heat of solution of argon over the composition range from 0.985 to 0.75 mole fraction

of water. They interpret their data in terms of increasing the structure of the solvent. The range covered is not great enough to show the presence or absence of a maxima in this system. In work reported by Ben-Naim and Moran[7] the solubility of argon in mixtures of water-p-dioxane have been determined. The results of this work are explained in terms of p-dioxane destabilizing the structure of the water. The calculated heat of solution of argon does not exhibit a maxima in this system, however.

All of the above studies are concerned with data obtained in systems where one component of the solvent is water. The results all point out that methanol, ethanol, and triethylamine have a structure-forming influence on water at compositions of about 70-85 mole per cent water. Dioxane probably has a structure-destabilizing effect, however. The heats of solution are similar, except for argon, in systems containing water.

Investigations on solubilities and heats of solution of electrolytes in mixtures of methanol-ethanol have been reported. Samoilov, Rabinovich, and Dudnikova[8] have reported solubility data for sodium chloride. They observed a maximum in the solubility of sodium chloride in the methanol rich region of the solvent and a minimum in the solubility of sodium chloride in the ethanol rich region of the solvent. They interpret their data in terms of stabilization and break down of the structure of the solvent. Stabilization of the solvent structure occurs when the molecules of the solute fit within "holes" in the liquid structure. Break down of the structure occurs when the solute molecules are too large in

size and shape to fit within the holes. There is no mention in the article as to the amount of sodium chloride in the ionized form.

Krestov and Klopov[9] have determined the heat of solution at infinite dilution of calcium nitrate in mixtures of methanol-ethanol. They report a maximum in the heat of solution in the region containing predominantly ethanol and a minimum in the region containing predominantly methanol. They explain their results in the same manner as Samoilov and his group, also without any mention of the amount of ionization of the calcium nitrate, though complete ionization is normally assumed at infinite dilution.

III. Experimental

A. Materials:

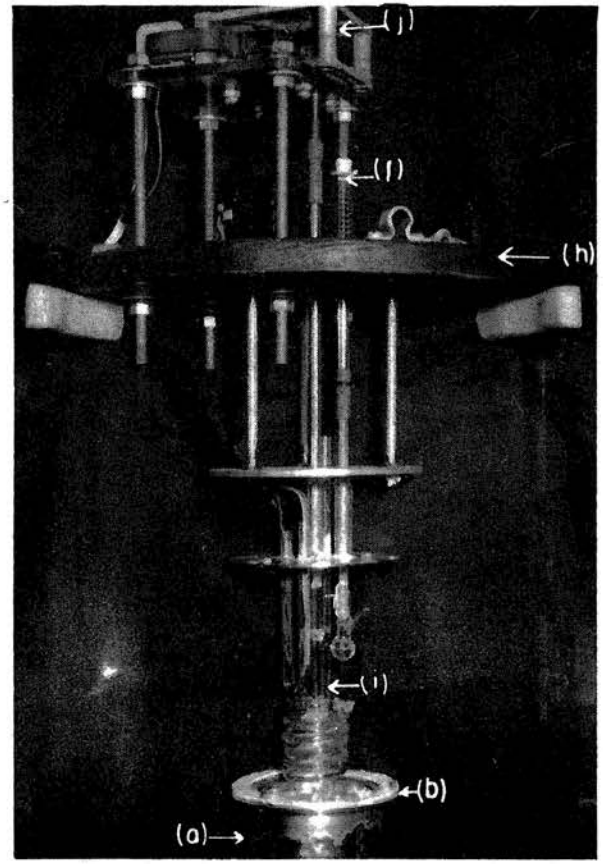
The methanol, isopropanol, and acetone used in this investigation were Matheson, Coleman and Bell Spectro-quality reagent grade and the chloroform and n-butanol were Matheson, Coleman and Bell Chromato-quality and were used without further purification. Several different lots of the solvents were used in the course of this work. There were no discernible variations in the properties measured that could be attributed to use of different lots of either solvent.

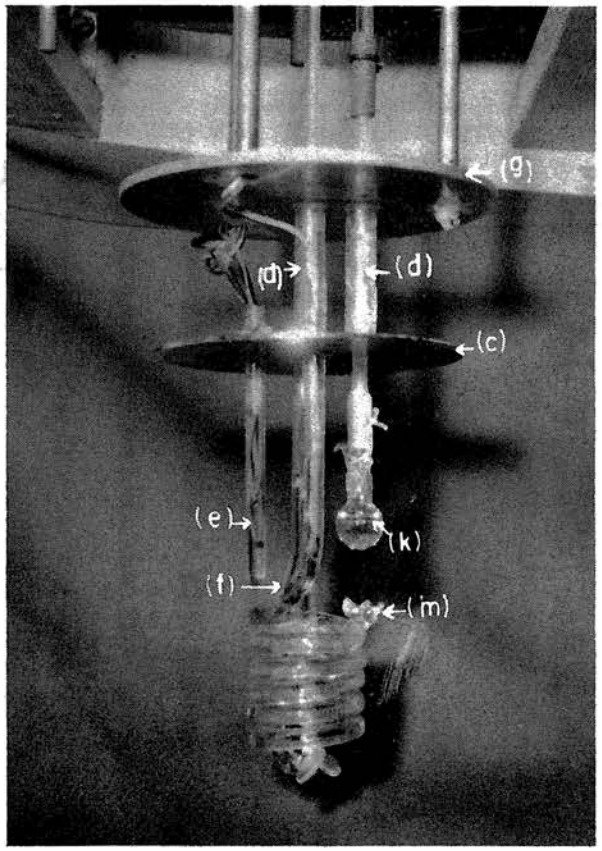
The water used was distilled once through an all glass distilling apparatus. Further purification appeared to have no effect on the measured heat of solution. In the measurement of the apparent partial molar excess volume, the most consistent results were obtained when the water was freshly boiled to remove any dissolved gases. It was also necessary to use freshly boiled chloroform to prevent the formation of air bubbles in the measurement of the apparent partial molar excess volume of chloroform.

B. Apparatus:

1. Calorimeter [10] (fig. 1):

The calorimeter consists of a silvered glass Dewar flask (a) of about 300 ml capacity with a chrome plated brass flange secured to it with epoxy cement. The flange, with a silicone rubber (b) gasket, bolts to a chrome plated brass lid (c). The lid has two 5mm i.d. Trubore glass





a. Dewar flask
b. gasket
c. lid
d. glass bearings
e. tube for thermistors
f. spiral glass tube-heater
g. aluminum plate
h. wood plate
i. stirrer
j. stirring motor
k. sample bulb
1. breaker shaft
m. spur

Figure 1. Calorimeter

bearings (d), a glass tube for the thermistors (e), and a spiral glass tube (f) for the heater cemented to it. The lid is suspended by the glass bearings from an aluminum plate (g), and this plate is suspended from a larger wood plate (h). The wood plate serves as a mount for the stirring motor. The entire unit is surrounded by a metal submarine which bolts to the wood plate and is suspended in an oil bath. The solution in the Dewar flask is stirred by glass impellors on a glass Trubore shaft (i), driven by a 500 rpm stirring motor (j). Samples of solute are weighed into fragile glass bulbs (k) of various capacities dependent on the sample size, and sealed by closing off the side arm. These bulbs are tied onto the breaker shaft (l). During the experiment the reaction is initiated by depressing the breaker shaft and causing the bulb to be crushed when it strikes the spur (m) mounted on the heating coil. It was found that crushing a bulb filled with liquid of the same composition as that contained in the Dewar flask absorbs 0.02, $\pm$ 0.02 calories. All calorimetric measurements were corrected for this effect.

The heat capacity of the calorimeter is determined with a 325.74 ohm bifilarly wound maganin heater, mounted in the glass spiral (f), filled with transformer oil. Current is supplied to the heater by a Heathkit Model IP-20 regulated power supply, operating at 18 volts.

The thermometer circuit consists of two thermistors (YS1, 10,000 ohms at 25°C.) comprising opposite arms of a Maier bridge circuit[11]. The other arms consist of fixed 10,000 ohm resistors. (fig. 2)

During an experiment the bridge input potential is kept constant at 1.0000 volt. The potential across the bridge circuit is monitored by a Leeds and Northrup K-3 Universal Potentiometer and the null position determined by a Hewlett Packard 419A D.C. Null Voltmeter. The out of balance potential of the bridge circuit is determined with a Keithley Model 660A Differential Voltmeter with a sensitivity of 2 microvolts.

2. Dilatometers:

For this portion of the investigation, two dilatometers (fig. 3) were constructed in the laboratory. The two differed in the sizes of the sample chambers, so that large or small samples could be used depending on the magnitude of the volume change. The body (a) of the dilatometer was constructed with a slight bend so that the sample could be trapped in the arm by mercury (c). The body of the dilatometer was fitted with a standard taper 10/30 ground glass joint (d). The male member of the joint has attached to it a precision capillary tube with a bore of about 0.05 cm. (e). The two portions of the dilatometer were held together firmly by rubber bands stretched over the glass hooks (f). During operation the height of liquid in the capillary tube

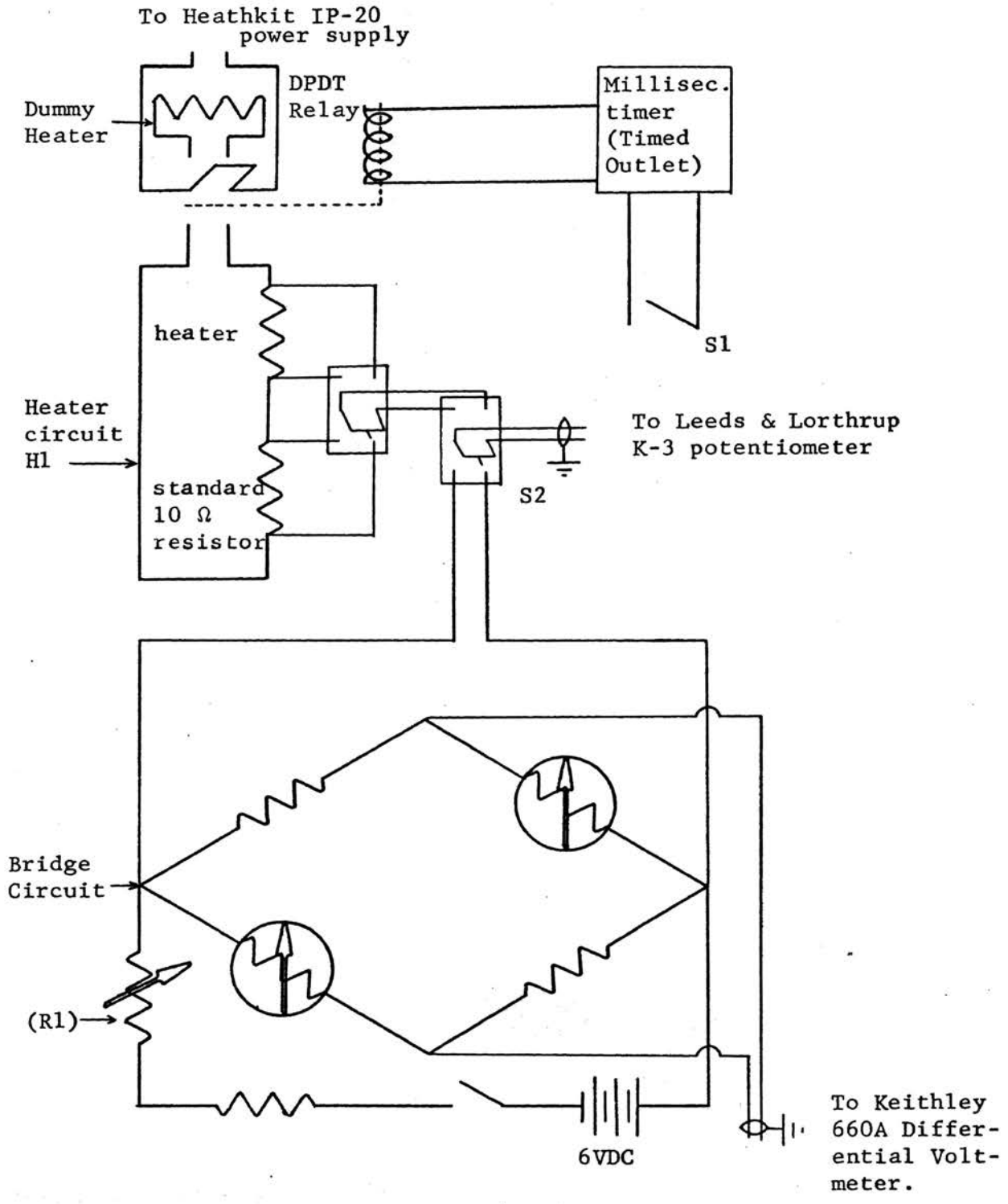


Figure 2. Circuit Diagram of Calorimeter.

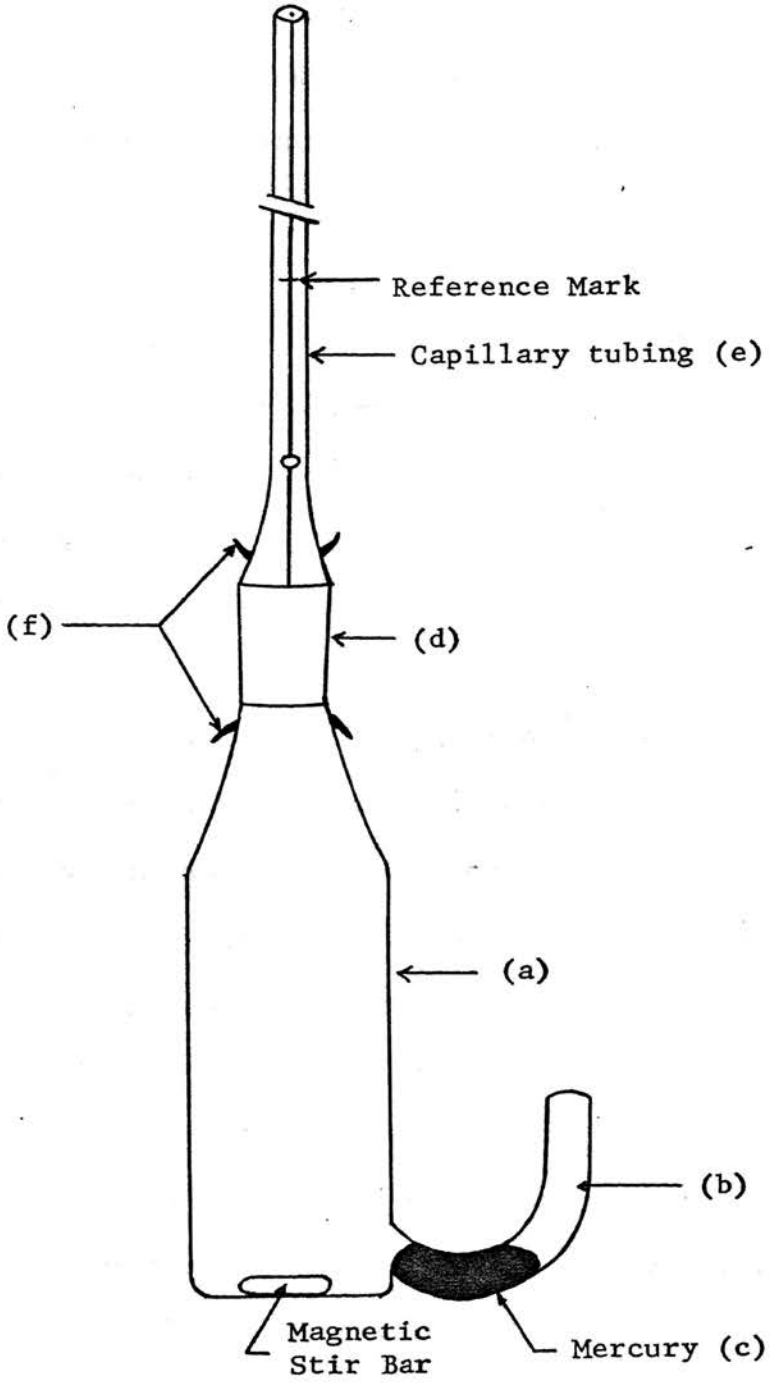


Figure 3. Dilatometer

was determined by a cathometer to 0.01 cm. The dilatometer was suspended in a constant temperature bath maintained at 25.00 $\pm$ 0.01°C by a Sargent, Model ST, Thermonitor temperature controller and was constant to within 0.002°C during an experiment. The temperature of the bath was monitored during each experiment by a Beckman thermometer, calibrated against a Platinium Resistance Thermometer calibrated by the National Bureau of Standards.

C. Experimental Procedure:

1. Calorimetry:

a. Preparation Procedure:

A weighed sample bulb was filled with solute, sealed, and the weight of sample determined by difference. The amount of solute to be used in the experiment was determined by the amount of heat expected from the reaction. The solute was generally chosen to give a heat effect of slightly over 10 calories since this is in the range of greatest sensitivity. In those cases where the heat effect was very small the sample size was limited to about 8 ml by the design of the calorimeter. A hypodermic syringe was used to inject the sample into the bulb (fig. 1) through the side arm. Glass tubing was inserted into side arm after filling and the side arm sealed with a flame. The sample bulb was allowed to cool to room temperature and weighed to 0.01 mg. The sample

bulb was tied securely with thread to the breaker shaft.

Solvent of the desired composition was prepared by pipetting the requisite volume of each component into a 500 ml flask and then weighing to 0.1 g. The solvent temperature was adjusted to about 24.0°C, approximately 300 mls pipetted into the Dewar flask, and the weight of solvent determined by difference. The Dewar flask was bolted to the calorimeter lid and the submarine bolted around it. The entire unit was suspended in a constant temperature bath filled with transformer oil at 25.0° ± 0.2°C. The electrical connections were made and the calorimeter allowed to thermally equilibrate for one hour. During the equilibration period the temperature inside the Dewar flask was adjusted to the appropriate starting temperature by operation of the heater. It had been determined previously that 25.0°C gave a reading of -1700μv on the differential voltmeter. To determine this value, the temperature sensing part of the calorimeter (e) was submerged in a water bath. The temperature of the water was measured and the out of balance potential of the bridge determined at that temperature. This procedure was repeated for a number of temperatures, below and above 25.0°C. The change in temperature in microvolts was fitted to equation 1.

$$(t - 25.0^{\circ}) = 52.24\ (1700 + E_{Br})\ 10^{-6},\ \pm 0.02^{\circ}C \quad (1)$$

In equation 1, E_{Br} is the out of balance potential of the bridge (in microvolts) and t is the temperature in centigrade degrees. The starting temperature for the experiment was chosen so that the temperature change would cause the differential voltmeter deflection to cross -1700μv.

b. Measurement Procedure:

At the start of the experiment switches are closed completing the circuits to the Maier bridge and potentiometer so that the batteries and circuit components have 45-60 minutes to stabilize thermally and electrically. At this time the power switches for the differential voltmeter and the null voltmeter are turned on, since these require 30-45 minutes to warm up. Switches S1 and S2 (fig. 2) are in the down position; heater off, potentiometer across bridge circuit.

When the equilibration was complete the bridge potential was adjusted to 1.0000 volt by adjusting resistor (R-1). Since the calorimeter was not completely adiabatic, compensation was made for the flow of heat between the system and surroundings by determining the rate of change of the temperature of the system due to the heat leak and extrapolating these "drift" rates from before and after the process to the point in time at which one half of the heat of the process had been detected.

The differential voltmeter determines the out of balance potential of the Maier Bridge. By observing and recording the change in potential at constant time intervals (one minute) the drift rate was determined. Switches S1 and S2 were placed in their uppermost positions. Switch S1 supplies power to the timer and energizes a relay which completes the heater circuit (Fig. 2, H1). Switch S2 transfers the potentiometer from the bridge circuit to the standard 10 ohm resistor. The potential drop across the standard resistor was determined several times and the values obtained were averaged for the determination of the heat capacity. Current was supplied to the heater circuit for one or two minutes, depending on the amount of heat expected from the solution process. Switches S1 and S2 were returned to their former positions and the time that current had been flowing was recorded. The potential across the bridge circuit was again adjusted to 1.0000 volts and the deflections of the differential voltmeter were recorded until the drift rate was determined to be constant. The sample was then introduced by depressing the breaker shaft (fig. 1, 1). After the drift rate was again constant the heat capacity determination was repeated as described previously. After the heat capacity determination, all switches were returned to their starting positions. The calorimeter was then prepared for another experiment.

2. Dilatometry:

The cross-sectional area of the capillary tube was determined by filling a portion of it with mercury. The length and weight of the column of mercury was determined. From the weight and density of the mercury the volume was determined and by dividing the volume by the length, the cross sectional area of the capillary tube was obtained.

About 60 ml of solvent mixture was prepared by pipetting the required amount of each component into a flask and weighing to 0.1g. The sample chamber of the dilatometer was filled with clean mercury and a small magnetic stirring bar placed in the body of the dilatometer. The weight of the dilatometer was obtained to 0.01 mg. Solute was placed in the sample chamber of the dilatometer and the sample trapped in place by the mercury (fig. 3). The excess sample was evaporated from the body of the dilatometer by passing air through it. The weight of the dilatometer with the solute was determined. The dilatometer was filled with the solvent and the capillary fitted into place. The dilatometer was suspended in a constant temperature bath. The height of the liquid in the capillary was adjusted and the dilatometer allowed to thermally equilibrate for one hour. After equilibration, the height of the liquid in the capillary relative to a reference mark on the stem was observed and recorded at 10 minute intervals. After 30 minutes, during which the

height of the liquid in the capillary remained constant, the dilatometer was removed from the constant temperature bath and the contents were mixed by tilting the dilatometer to spill the mercury out of the sample chamber. To insure thorough mixing the small magnetic stirring bar was operated at high speed for 2-3 minutes. The dilatometer was returned to the constant temperature bath and again allowed to equilibrate. The height of the liquid in the capillary was observed and recorded at 10 minute intervals until it was determined to be constant. The dilatometer was then removed from the constant temperature bath and prepared for another experiment.

Since the capillary tube was at room temperature rather than the bath temperature, it was felt that it would be necessary to correct the observed height change for this temperature difference. This correction was made and found to have negligible effect on the apparent partial molar volume.

D. Calculations:

1. Calorimetry:

The calorimeter has an internal calibrating heater built into it. The heater was constructed from manganin wire which has a negligible change in resistance with temperature. The resistance of the heater was determined relative to a standard resistance. The resistance value of the heater was checked periodically during this work and changed by 0.04% over an eight month period.

The heat capacity of the system was determined by observing the change in the out of balance potential of the Maier bridge resulting from the input of a measured quantity of electrical energy. The time that current was being supplied to the heater and the potential drop across a standard 10 ohm resistor in series with the heater was determined. From these quantities the heat capacity given by equation 2 was determined.

$$C = \frac{q_h}{\triangle E_h} \tag{2}$$

In equation 2, C is the heat capacity of the system, $\triangle E_h$ is the change in temperature of the system obtained from the out of balance potential of the Maier bridge in microvolts, and q_h is the electrical heat in calories produced by the flow of current (I) through a resistance (R_h) for a time (t, sec.). q_h was determined from equation 3.

$$q_h = \frac{I_h^2 R_h t}{4.184} \tag{3}$$

The current through the heater (I_h) can be obtained from the potential drop (E_s) across the 10 ohm standard resistor. The potential drop (E_s) is related to the current (I_h), since the standard 10 ohm resistor is in series circuit with the heater. In a series circuit the current flowing is the same in all points of the circuit and from Ohm's Law

$$I_h = \frac{E_h}{R_h} = I_s = \frac{E_s}{R_s} \quad . \tag{4}$$

In equation 4, the subscripts (h) and (s) refer to the heater and the standard 10 ohm resistance respectively. Substituting the value of I_h from equation (4) into equation (2), equation 5 is obtained.

$$q_h = \frac{E_s^2 \; R_h \; t}{R_s^2 \; 4.184} \tag{5}$$

Since the value of the heater resistance and the standard 10 ohm resistance are constant they are grouped together with the factor for conversion of joules to calories into a factor

$$F = \frac{R_h}{R_s^2 \; 4.184} \quad . \tag{6}$$

The factor has a value of 0.77890 cal/ohm-joule. The final expression used to calculate the heat capacities was

$$q_h = E_s^2 \; F \; t \quad . \tag{7}$$

From independent measurements it had been determined that one half of the heat has been detected after about 60% of the heating period was completed. For a one minute heating period, the fore drifts and after drifts are extrapolated to a point in time, 0.6 minutes, after the heater was activated. The change in temperature in microvolts ($\triangle E$) was obtained by difference and is the heat effect of the flow of current through the heater. In table I and II

data obtained from a typical experiment and the calculations are presented. In Figure 4 the data is shown graphically.

The value calculated for the electrical heat is divided by ($\triangle$E) to give the heat capacity of the system in calories per microvolt. The heat capacity was determined before and after the solution process and the values obtained were averaged. This gives an average heat capacity over the range of temperature at which the solution process occurs.

The ($\triangle$E) for the reaction was calculated in a similar manner as the ($\triangle$E) for the heat capacity determination. This ($\triangle$E) was multiplied by the average heat capacity and the result was the heat effect due to the solution process in calories, (q). The observed heat was corrected for the heat effect of breaking a sample bulb. The corrected heat effect is divided by the number of millimoles of solute to obtain the heat effect for one gram molecular weight of solute in a large amount of solvent.

2. Dilatometry:

In table III the data that was obtained from a typical experiment is given. The number of millimoles of solute were divided into the cross sectional area of the capillary tubing. The value obtained was multiplied by the change in height of the liquid in the capillary to obtain the change in volume on mixing. If the change in volume,

TABLE I

EXPERIMENTAL DATA, CALORIMETRY

Page 146 Book 2 Acetone (2nd Sample) Solvent Make Up
(100 mls IprOH 78.6)
27 June 1968 (250 mls meOH 196.8)

F = 0.77890 Wt. of bulb + solute 2.67502
Mw = 58.08 Wt. of empty bulb 1.89143
10^3n = 13.491 moles Wt. solute 0.78359 gm. Wt. solvent 220.5gm.

Bath Temperature 24.6°C

Time		$-E_{Br}$ (Differential Voltmeter Reading)
0.		2587
1.		2616
2.		2645
3.		2671
4.		2698
5.	heater on	2724
	heater time 60.06 sec.	Es = .54963
		.54954
		.54958
6.	heater off	
7.		0956
8.		0979
9.		1009
10.		1039
11.		1066
12.		1093
13.	sample bulb crushed	1120
14.		2499
15.		2515
16.		2530
17.		2545
18.	heater on	2560
	heater time 59.99 sec.	Es = .54930
		.54939
		.54946
19.	heater off	
20.		0778
21.		0794
22.		0819
23.		0843
24.		0866
25.		0892

TABLE II

CALCULATIONS-CALORIMETRY

Page 147 Book T-2 $n = 13.491$ m moles

1st heat capacity determination

Time of reading	extrapolation point	reading μv	drift rate	extrapolated reading μv
5 min.		-2724	-26.3 $\frac{\mu v}{min}$	-2740
	5.6			
8 min.		-0979	28.2	-0911

temperature change $\Delta E = 1829\mu v$

$$q_n = E_h^2 F t = (.54958)^2(.77890)(60.06 \text{ sec.}) = 14.13 \text{ calories}$$

$$C = \frac{q_h}{\Delta E} = 0.7725 \times 10^{-2} \text{ cal}/\mu v$$

Time of reading	extrapolation point	reading μv	drift rate	extrapolated reading μv
18 min.		-2560	15.2 $\frac{\mu v}{min}$	-2569
	18.6			
21 min.		-0794	24.5	-0735

$\Delta E = 1834\mu v$

$$q_h = (.54938)^2(.77890)(59.99) = 14.10 \text{ calories}$$

$$C = \frac{q_h}{\Delta E} = 0.7690 \times 10^{-2} \text{ cal}/\mu v$$

$$C_{ave.} = 0.7798 \times 10^{-2} \text{ cal}/\mu v$$

Process;

Time of reading	extrapolation point	reading μv	drift rate	extrapolated reading μv
13 min		-1120	27 $\frac{\mu v}{min}$	-1134
	13.5			
14 min.		-2499	15.2	-2491

$\Delta E = 1357\mu v$

$q = \Delta E \cdot C_{ave} = 10.46$ calories

Correction for bulb breaking = -0.02 calories

q corr = 10.44 calories

$$\Delta H = \frac{q \text{ corr}}{n} = +0.774 \text{ kcal/mole}$$

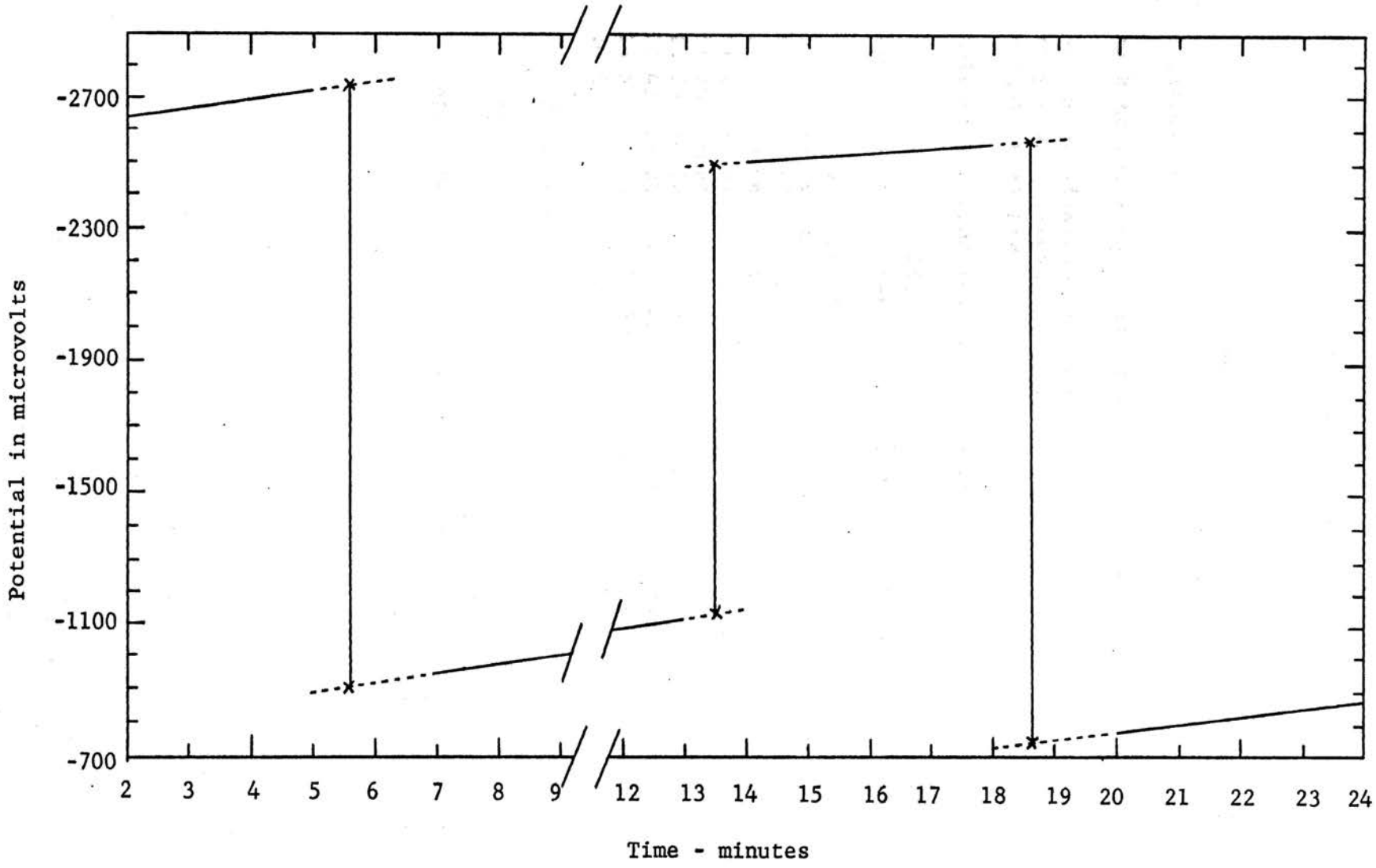


Figure 4. Experimental Data, Calorimetry

TABLE III

EXPERIMENTAL DATA - DILATOMETRY

Page 231 Book T-2

Solute-Acetone Solvent-Isopropanol (X_i = 1.000)

Dilatometer B

Mark height above water level 24.5 cm

Weight of dilatometer with sample 58.72303
Weight of dilatometer empty 58.33924
Weight of sample 0.38379 gm

Molecular weight solute 58.08 number of moles solute 6.608×10^{-3}

Time	mark height	liquid height	(l-m)	stem temperature	average height	change in height
9:00	placed in bath					
10:55	13.99 cm	13.24 cm	-0.75 cm	27.8°C		
11:05	13.82	12.94	-0.88	28.0		
11:15	13.96	13.13	-0.83	28.1	-0.86 cm	
11:27	13.71	12.85	-0.86	28.1		
11:30	mixed					+5.13 cm
13:29	14.26	18.53	4.27	28.9		
13:45	14.09	18.44	4.35	29.1		
13:55	15.25	19.59	4.24	29.0	4.27	
14:04	15.37	19.59	4.25	28.1		

Cross sectional area of capillary bore: $1.854 \times 10^{-3} cm^2$

Change in volume: $(1.854 \times 10^{-3} cm^2 \times 5.13 cm) = 9.51 \times 10^{-3} ml$

Apparent partial molar excess volume: $\frac{9.51 \times 10^{-3} ml}{6.608 \times 10^{-3} mole} = 1.44 \frac{ml}{mole}$

ΔV, was constant to within $\pm$ 0.02 ml/mole the observed values were averaged and this value taken as the apparent partial molar excess volume at infinite dilution. For changes in volume that showed a deviation greater than $\pm$ 0.02 ml/mole on two successive samples, at least one more solute sample was added to the solvent and the values obtained were extrapolated to infinite dilution.

IV. Theory

A. General Considerations, Enthalpy Changes:

In considering the solution process, distinction must be made between the integral or total heat of mixing and the differential heats of solution. The integral heat of mixing process can be represented as

$$n_A\ A_{(1)} + n_B\ B_{(1)} \xrightarrow{T,P} (n_A\ A \cdot n_B\ B)_{sol'n} \quad . \qquad \text{I}$$

In this process n_A and n_B refer to the number of moles of components A and B respectively. The change in enthalpy for this process is given by

$$\Delta H^{mix} = n_A(\bar{H}_A - \bar{H}_A^{\triangle}) + n_B(\bar{H}_B - \bar{H}_B^{\triangle}) \quad . \qquad (8)$$

In this equation, the quantities $\bar{H}_A$ and $\bar{H}_B$ refer to the partial molar enthalpies of components A and B in solution and the superscript ($\triangle$) refers to the pure components. The partial molar enthalpies are defined by[12]

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j\ j\neq i} \quad . \qquad (9)$$

The heat of solution can be represented by the process

$$S_{(1)} + n_B\ B_{(1)} \xrightarrow{T,P} (S \cdot n_B\ B)_{sol'n} \quad . \qquad \text{II}$$

This process is a special case of I. The change in enthalpy for this process is given by the equation

$$\Delta H = (\bar{H}_S - \bar{H}_S^{\triangle}) + n_B(\bar{H}_B - \bar{H}_B^{\triangle}) \quad . \qquad (10)$$

The final process to be considered is represented by

$$A_{(l)} + \begin{bmatrix} n_A A \\ n_B B \end{bmatrix}_{sol'n} \xrightarrow{T,P} \begin{bmatrix} (n_A+1)\ A \\ n_B \quad\ B \end{bmatrix}_{sol'n} \qquad \text{III)}$$

The enthalpy change for this process is given by the equation

$$\Delta H = n_A(\bar{H}_A' - \bar{H}_A) + n_B(\bar{H}_B' - \bar{H}_B) + \bar{H}_A' - \bar{H}_A^{\Delta} \quad . \qquad (11)$$

In equation (11) the superscript (') refers to the partial molar enthalpies of the components in the final solution. The heat of this process (III) is referred to as the differential heat of solution if the amount of the solvent is very large, such that the final composition is essentially the same as the initial composition. As n_A and n_B become much greater than one, equation (11) can be reduced to

$$\Delta H = n_A d\bar{H}_A' + n_B d\bar{H}_B' + \bar{H}_A' - \bar{H}_A^{\Delta} \quad . \qquad (12)$$

From the Gibbs-Duhem relationship

$$n_A d\bar{H}_A + n_B d\bar{H}_B = 0 \quad , \qquad (13)$$

equation (12) becomes

$$\Delta H = \bar{H}_A' - \bar{H}_A^{\Delta} \quad . \qquad (14)$$

Since it is impossible to determine the absolute enthalpy of a substance and measurements give the change in enthalpy in going from one state to some other state, a reference state can be chosen and the change in enthalpy determined relative to the reference state. Lewis and Randall[13] have defined a quantity, $\bar{L}$, referred to as the relative partial molar enthalpy by

$$\Delta H = (\bar{H}_A - \bar{H}_A^{o}) = \bar{L}_A \quad . \qquad (15)$$

The superscript (°) refers to the standard state, which in this work is chosen as the pure liquid. The reference state is chosen as the pure liquid in either case and subtraction of the reference state enthalpies from equation (15) gives

$$\Delta H = (\bar{H}_A' - \bar{H}_A^o) = \bar{L}_A \quad . \tag{16}$$

In process III, component B could have been chosen for the solute and by a similar treatment $\bar{L}_B$ is obtained,

$$\Delta H = (\bar{H}_B' - \bar{H}_B^o) = \bar{L}_B \quad . \tag{17}$$

In process I, the enthalpies of the pure liquids are subtracted from equation (8) to give

$$\Delta H^{mix} = n_A\bar{L}_A + n_B\bar{L}_B \quad . \tag{18}$$

Referring to process II, if the amount of solvent (B) is very much greater than the amount of solute (S), the enthalpy of the solvent is the same in the initial and final states,

$$\bar{H}_{B(i)} = \bar{H}_{B(f)} \quad , \tag{19}$$

and equation (10) becomes

$$\Delta H^{sol'n} = (\bar{H}_S - \bar{H}_S^{\Delta}) \quad . \tag{20}$$

B. Experimental Considerations:

1. Differential Heats of Solution:

The heats of solution of small amounts, less than 8 ml, of the pure components have been determined in relatively much larger amounts of solvent mixtures and the

pure components, approximately 300 ml, over a broad range of compositions. Process II is considered to represent these measurements. Since the change in composition is small, less than 0.010 mole fraction, the heat affects observed can be considered to approximate the differential heat of solution of the solute. The relative partial molar heats were plotted versus composition and a smooth curve drawn through the points to give the $\bar{L}$'s over the whole composition range. Since both components of the solvent were used as solutes the $\bar{L}$ curves of methanol and isopropanol were obtained.

2. Heats of Mixing:

The values of the heat of mixing of methanol and isopropanol were obtained by calculation from the ($\bar{L}$'s). To obtain the heat effect of formation of one mole of solution equation 18 is divided by $(n_A + n_B)$ to give

$$\Delta\bar{H}^{mix} = x_A\bar{L}_A + x_B\bar{L}_B \quad . \tag{21}$$

3. Heats of Solution at Infinite Dilution:

The heat of solution at infinite dilution is defined such that the solute is dissolved in such a large quantity of solvent that the addition of more solvent produces no additional heat effect. In this investigation the heats of solution of successive small portions of solute, sample volume ranging from 0.1 ml to 3 ml, in much larger amounts of solvent, 300 ml, were determined. The measured values

are considered to be represented by process II and the enthalpy of the process is obtained from equation 20. The heat effects observed for successive samples of acetone and n-butanol going into solution were constant to within experimental error. The heat effects observed for successive samples of chloroform and water exhibited a consistent deviation. These values were plotted versus the number of moles of solute and extrapolated to infinite dilution.

C. General Considerations, Volume Changes:

Initially the dilatometer contained pure solute, a relatively much larger volume of solvent, and a quantity of mercury. The total initial volume may be represented by

$$V_i = (n_s\bar{V}_s + n_A\bar{V}_A) + V_{Hg} + n_A'\bar{V}_A^{\Delta} \quad . \tag{22}$$

$(n_s\bar{V}_s + n_A\bar{V}_A)$ represents the volume of the solvent. This form is used since successive amounts of pure solute were mixed into the same solvent. $n_A'\bar{V}_A^{\Delta}$ represents the volume of the pure solute trapped in the sample arm by the volume of mercury, V_{Hg}.

The apparent partial molar volume is defined by

$$\Phi\bar{V}_A = \frac{V - n_s\bar{V}_s^{\Delta}}{n_A} \quad . \tag{23}$$

Rearranging equation (23) gives

$$V = n_A\,\Phi\bar{V}_A + n_s\bar{V}_s^{\Delta} \quad . \tag{24}$$

An alternative representation of the initial volume is

$$V_i = (n_s\bar{V}_s^{\Delta} + n_A\Phi\bar{V}_A) + V_{Hg} + n_A'\bar{V}_A^{\Delta} \quad . \tag{25}$$

After mixing, the volume of the final solution is

$$V_f = n_s \bar{V}_s + (n_A + n'_A)\, \bar{V}'_A + V_{Hg} \quad , \tag{26}$$

which can also be represented as

$$V_f = n_s \bar{V}^{\Delta}_s + (n_A + n'_A)\, \phi\bar{V}'_A + V_{Hg} \quad . \tag{27}$$

The volume change on mixing obtained by subtracting equation (25) from (27) is

$$\Delta V^{mix} = V_f - V_i = (n_A - n'_A)\phi\bar{V}'_A - n_A\phi\bar{V}_A - n'_A\bar{V}^{\Delta}_A \quad . \tag{28}$$

By dividing equation (28) by n'_A and rearranging, equation (29) is obtained.

$$\frac{\Delta V^{mix}}{n'_A} = \frac{n_A}{n'_A}(\phi\bar{V}'_A - \phi\bar{V}_A) + \phi\bar{V}'_A - \bar{V}^{\Delta}_A \tag{29}$$

As the number of moles of solute becomes small, equation (29) becomes in the limit

$$\lim_{n_A \text{ and } n'_A \to o} \frac{\Delta V^{mix}}{n'_A} = \phi\bar{V}_A - \bar{V}^{\Delta}_A \tag{30}$$

As the solution becomes infinitely dilute ($n_A \to o$) the limitting value of $\phi\bar{V}_A$ becomes $\bar{V}^{*}_A$ [15], which is the partial molar volume of A in an infinitely dilute solution and is not necessarily the same as the partial molar volume of pure A.

An excess thermodynamic property is defined such that

$$J^e = J_{real} - J_{ideal} \quad .^{16} \tag{31}$$

The partial molar excess volume is defined as the volume

exhibited by the pure liquid solute (ideal partial molar volume) subtracted from the volume exhibited by the solute in the infinitely dilute solution;

$$\bar{V}_A^{*e} = \bar{V}_A^{*} - \bar{V}_A^{\Delta} = \lim_{n_A \to o} \frac{\Delta V^{mix}}{n_A} \quad . \tag{32}$$

D. Experimental Considerations, Apparent Partial Molar Excess Volumes:

The measurement of the change of volume on mixing of successive small portions of solute, 0.1 ml to 0.5 ml, in approximately 50 ml of solvent gave values for chloroform and n-butanol that were constant to within experimental error, $\pm$ 0.02 mls. The volume changes observed for water and acetone deviated in a consistant manner and were extrapolated to infinite dilution.

V. Results

A. Relative Partial Molar Heats and Integral Heats of Mixing:

The heats of solution of pure methanol and isopropanol were determined by introducing small amounts (1 to 8 ml) of the pure components into much larger quantities (300 ml) of solvents consisting of methanol, isopropanol, and mixtures of these components. In table IV the initial and final value of the compositions are given along with the observed heat effects. The heat quantities closely approximate relative partial molar enthalpies as was previously explained. The heat values are felt to be accurate to 2.0 per cent or 0.5 cal/mole, whichever is larger.

The integral heat of mixing curve for the methanol-isopropanol was calculated from smoothed curves of the $\bar{L}$ data at 0.05 mole fraction intervals from equation 21. The heat of mixing curve was fitted to an equation of the form

$$\Delta H^{mix} = x_i x_m \left[A + B\ (x_i - x_m)\right] . \tag{33}$$

The values obtained for A and B were 72.3 cal/mole and 28.2 cal/mole respectively. The $\bar{L}$ values were recalculated from the heat of mixing by the relations[13]

$$\bar{L}_i = \Delta H^{mix} + x_m \frac{\partial \Delta H^{mix}}{\partial x_i} ,$$

$$\bar{L}_m = \Delta H^{mix} - x_i \cdot \frac{\partial \Delta H^{mix}}{\partial x_i} . \tag{34}$$

The agreement between measured and calculated $\bar{L}$'s is good,

TABLE IV

EXPERIMENTAL VALUES OF THE RELATIVE PARTIAL MOLAR HEATS OF METHANOL AND ISOPROPANOL

Solute	Composition of Solution initial X_i	Composition of Solution final X_i	$\bar{L}_m$
MeOH	1.000	0.994	-103.2
"	0.994	0.981	-98.0
"	0.981	0.969	-95.7
"	0.969	0.956	-94.1
"	0.882	0.865	-64.6
"	0.865	0.846	-60.3
"	0.762	0.755	-43.1
"	0.682	0.671	-28.0
"	0.673	0.662	-27.0
"	0.493	0.486	- 9.7
"	0.136	0.133	0.0
"	0.096	0.094	0.0
			$\bar{L}_i$
IprOH	0.846	0.848	-4.0
"	0.760	0.762	-8.8
"	0.671	0.673	-13.5
"	0.680	0.682	-13.6
"	0.489	0.493	-26.3
"	0.292	0.299	-37.9
"	0.131	0.136	-43.9
"	0.126	0.131	-44.1
"	0.008	0.096	-44.4
"	0.008	0.017	-44.5
"	0.000	0.008	-44.6

however the calculated $\bar{L}$ into pure methanol disagrees with the extrapolated value by about 3.5 cal/mole. The additional precision obtainable from a three parameter equation is not warranted. The calculated values obtained for the $\bar{L}s^t$ were used to adjust the slopes of curves slightly and the integral heats of mixing recalculated. This process was repeated until a completely self consistent set of data was obtained. The consistency of the data is demonstrated by figure 5. The area under the curve of a plot of $(\bar{L}_i - \bar{L}_m)$ versus composition is equal within experimental error. This provides a test of internal consistency.[17] The area agrees to 3 parts per thousand. In table V and figure 6 the smoothed values of the relative partial molar enthalpies and the heats of mixing of methanol and isopropanol are presented. There was no data available in the literature with which to compare these results.

B. Heat of Solution at Infinite Dilution:

The heats of solution at infinite dilution of acetone, n-butanol, chloroform, and water have been determined in mixtures of methanol-isopropanol and the pure components. The measured values and compositions are presented in table VI, and in figure 7 these values are presented graphically. The values obtained in this investigation are considered to be accurate to within one per cent.

Some difficulty was experienced in obtaining reproducible heat of solution data for acetone. Reproducible results were

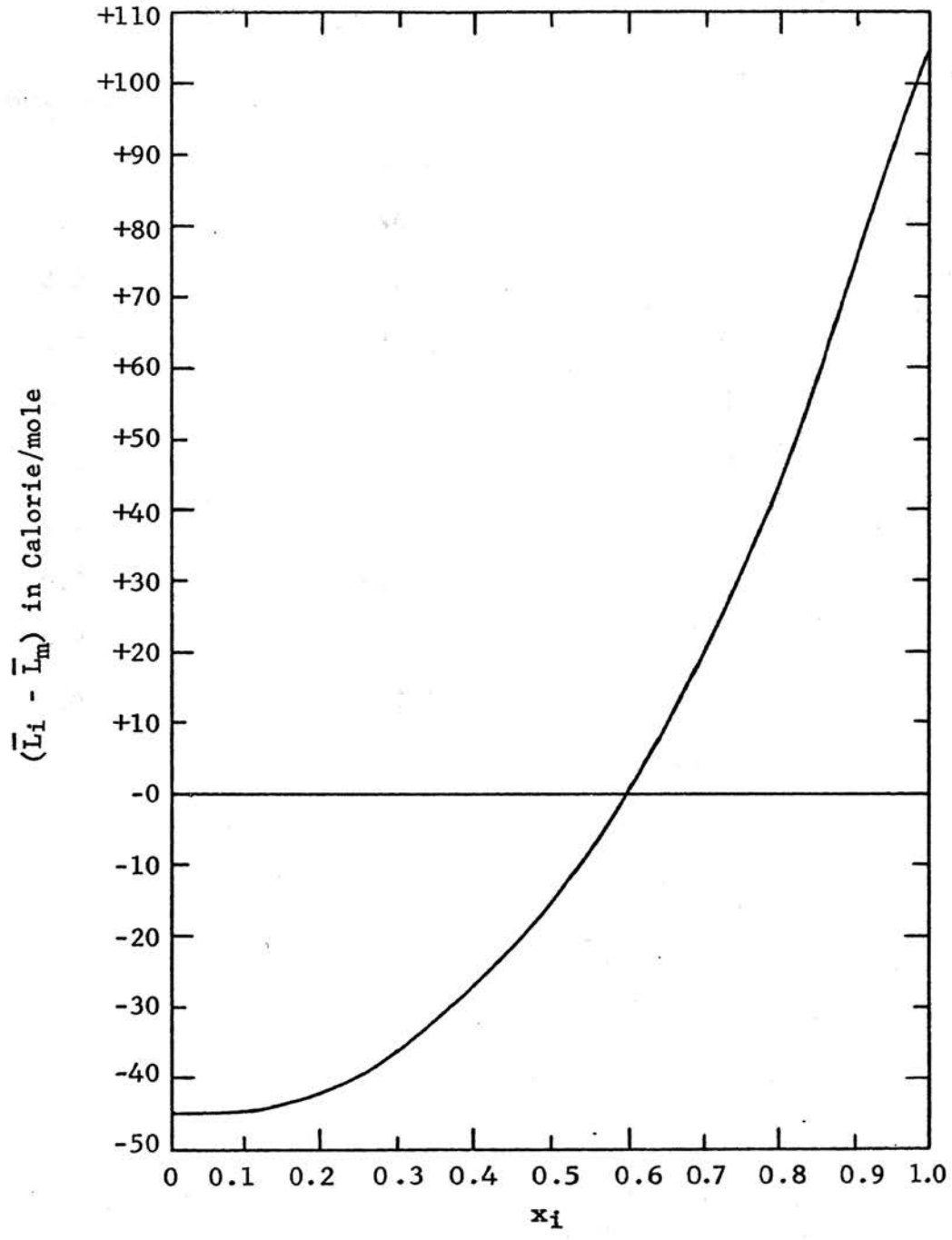


Figure 5. Test of Internal Consistency

TABLE V

SMOOTHED RELATIVE PARTIAL MOLAR HEATS AND
THE HEATS OF MIXING OF METHANOL AND ISOPROPANOL

Solvent	$\bar{L}_i$ cal/mole	$\bar{L}_m$ cal/mole	$\Delta_{mix}H$ cal/mole
0	-44.6	0	0
0.1	-44.0	0	-4.4
0.2	-42.2	-0.4	-8.8
0.3	-37.9	-2.0	-12.7
0.4	-31.3	-5.5	-16.1
0.5	-25.0	-12.0	-18.8
0.6	-18.2	-20.1	-19.1
0.7	-12.0	-32.5	-18.2
0.8	-6.2	-50.5	-15.2
0.9	-1.2	-72.0	-8.8
1.0	0	-104.5	0

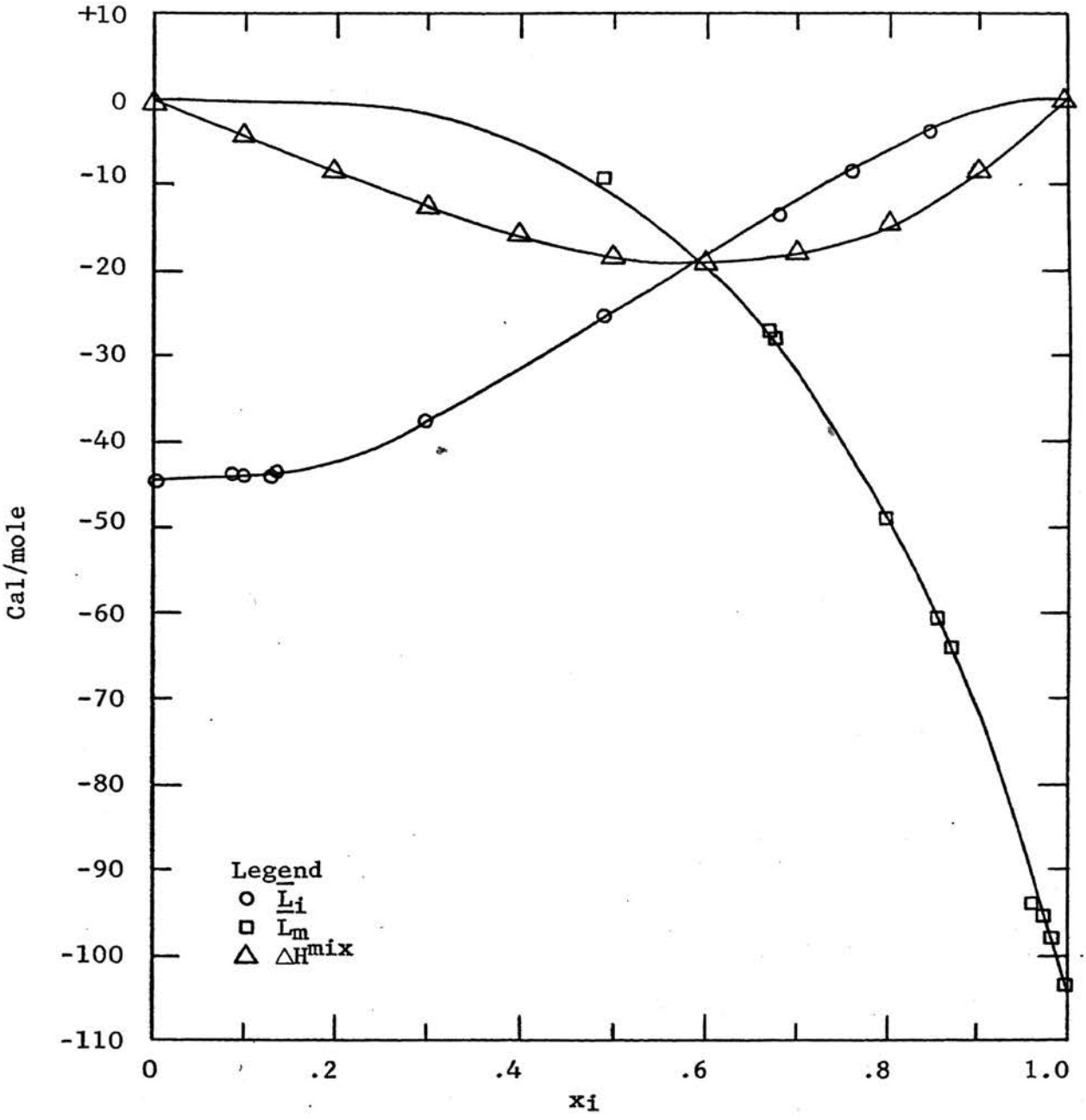


Figure 6. Relative Partial Molar Heats and the Heats of Mixing of Methanol-Isopropanol.

TABLE VI

HEATS OF SOLUTION AT INFINITE DILUTION

Solvent Solute x_i	Acetone	n-Butanol	Chloroform	Water
0.00_0	582 cal/mole	224 cal/mole	-1147 cal/mole	-718 cal/mole
0.01_7	608	---	---	---
0.08_1	670	---	-1190	-705
0.09_3	---	192	---	---
0.17_5	776	---	---	-672
0.22_7	---	---	-1260	---
0.25_0	---	---	---	-631
0.28_4	---	130	---	-604
0.29_9	928	---	---	---
0.34_5	---	---	-1287	---
0.39_8	---	---	---	-522
0.48_8	1182	83	-1299	-444
0.66_2	1422	---	---	---
0.67_9	1433	---	---	-220
0.74_0	---	31	-1186	---
0.75_5	---	---	---	-94
0.84_8	1690	---	---	---
0.87_6	---	---	---	125
0.88_2	1756	3	-1040	---
0.94_9	1865	---	---	---
1.00	1941	-23	-843	375

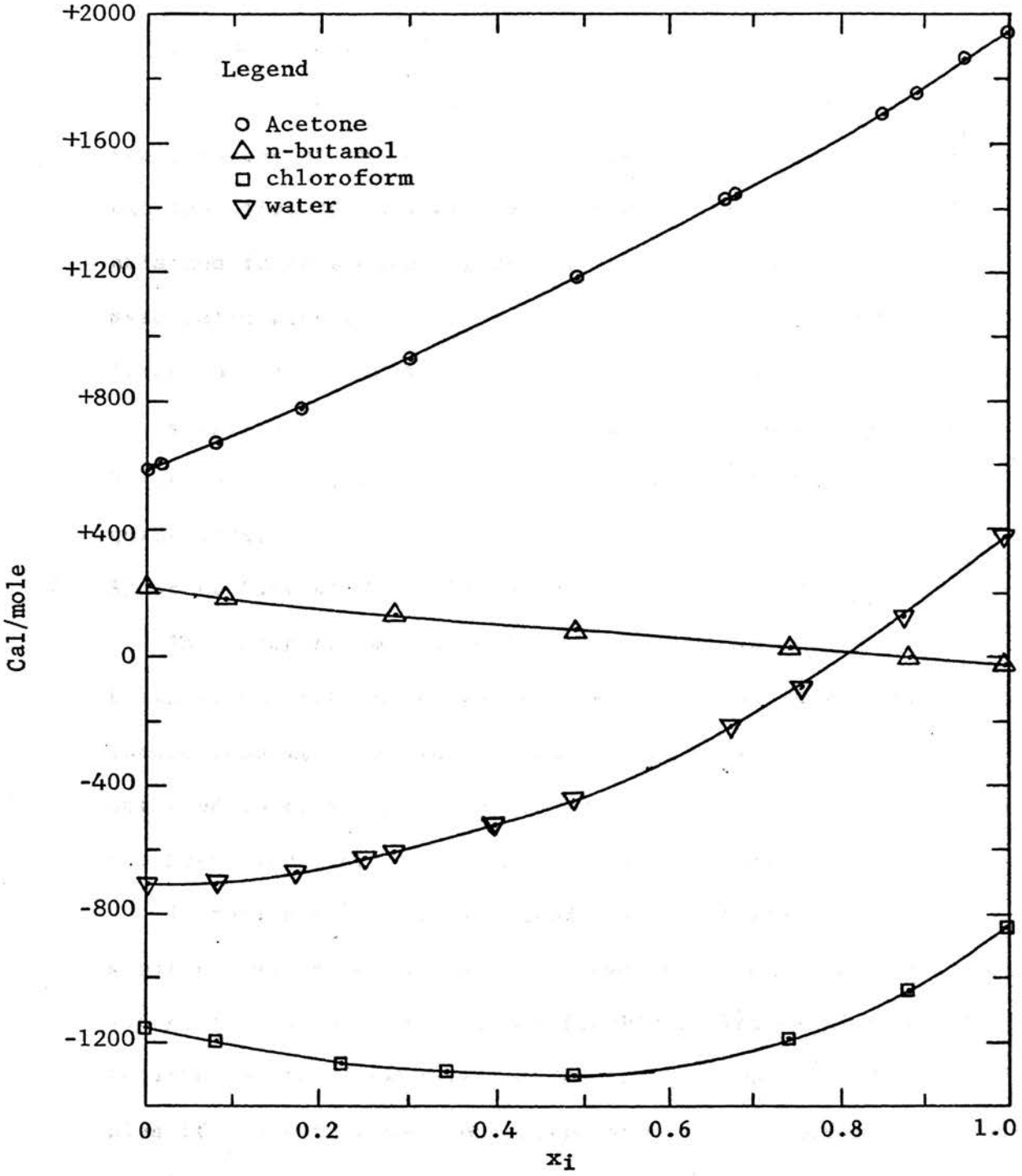


Figure 7. Heats of Solution at Infinite Dilution

obtained by cooling the acetone to 15°C or less immediately before filling the sample bulbs.

Not many values of the heat of solution at infinite dilution for non-electrolytes have been tabulated in the literature. However, values of the heat at infinite dilution can be obtained by extrapolation techniques from heat of mixing data. The values obtained in this manner generally have large uncertainties associated with them. In table VII the values obtained from the literature are tabulated along with the values obtained in this investigation. The values obtained in this investigation are believed to be the best values presently available for these quantities.

C. Apparent Partial Molar Excess Volumes.

The apparent partial molar excess volumes of acetone, n-butanol, chloroform and water were determined in methanol-isopropanol mixtures and the pure components. The values obtained in this investigation are tabulated in table VIII and are presented graphically in figures 8 and 8A.

To obtain reproducible results in the measurement of the apparent partial molar excess volume of the chloroform and water, it was necessary to use freshly boiled samples of solute. Erratic results were obtained due to the formation of air bubbles if the solute were not freed of dissolved gases.

In table IX the values from this investigation are presented along with those values obtained from the literature.

TABLE VII

COMPARISON VALUES FOR HEATS OF SOLUTION AT INFINITE DILUTION

Solute	Solvent	This work	Literature	Ref.	Method used to obtain Literature Value
water	methanol	-718 $\frac{cal}{mole}$	-719 $\frac{cal}{mole}$	2	a.
			-738	18	b.
water	isopropanol	375	400	19	b.
n-Butanol	methanol	224	227	20	b.
Chloroform	methanol	-1148	-789_{35^oC}	21	b.
Acetone	methanol	582	523	22	b.

a. Measurement of heat of solution near infinite dilution.

b. Extrapolation of heat of mixing data.

TABLE VIII

PARTIAL MOLAR EXCESS VOLUMES AT INFINITE DILUTION

Solvent	Solute			
x_i	Acetone	n-Butanol	Chloroform	Water
0.00	-1.71 ml/mole	0.57 ml/mole	-0.15 ml/mole	-3.75 ml/mole
0.03	-1.60	---	---	---
0.08	-1.50	---	-0.27	---
0.09	---	---	---	-3.95
0.13	---	0.45	---	---
0.17	-1.23	---	---	---
0.29	---	0.24	-0.70	-4.25
0.34	-0.89	---	---	---
0.48	-0.48	+0.09	-1.14	-4.34
0.51	---	---	---	-4.33
0.66	0.06	---	---	---
0.69	---	-0.06	---	-4.25
0.77	0.46	---	-1.57	---
0.88	0.89	-0.12	---	---
0.91	---	---	-1.76	-3.90
1.00	1.43	-0.15	-1.78	-3.58

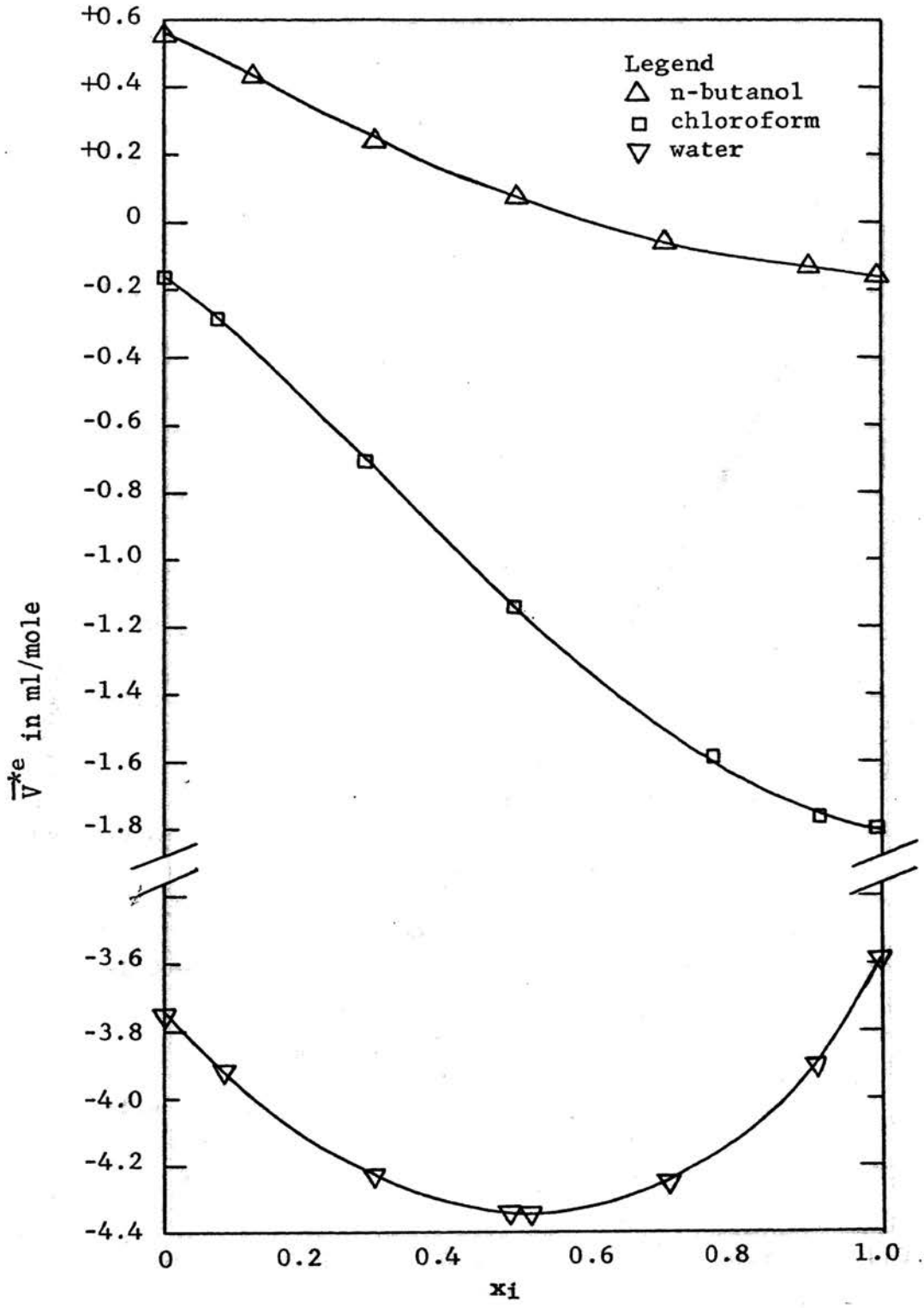


Figure 8. Partial Molar Excess Volumes at Infinite Dilution

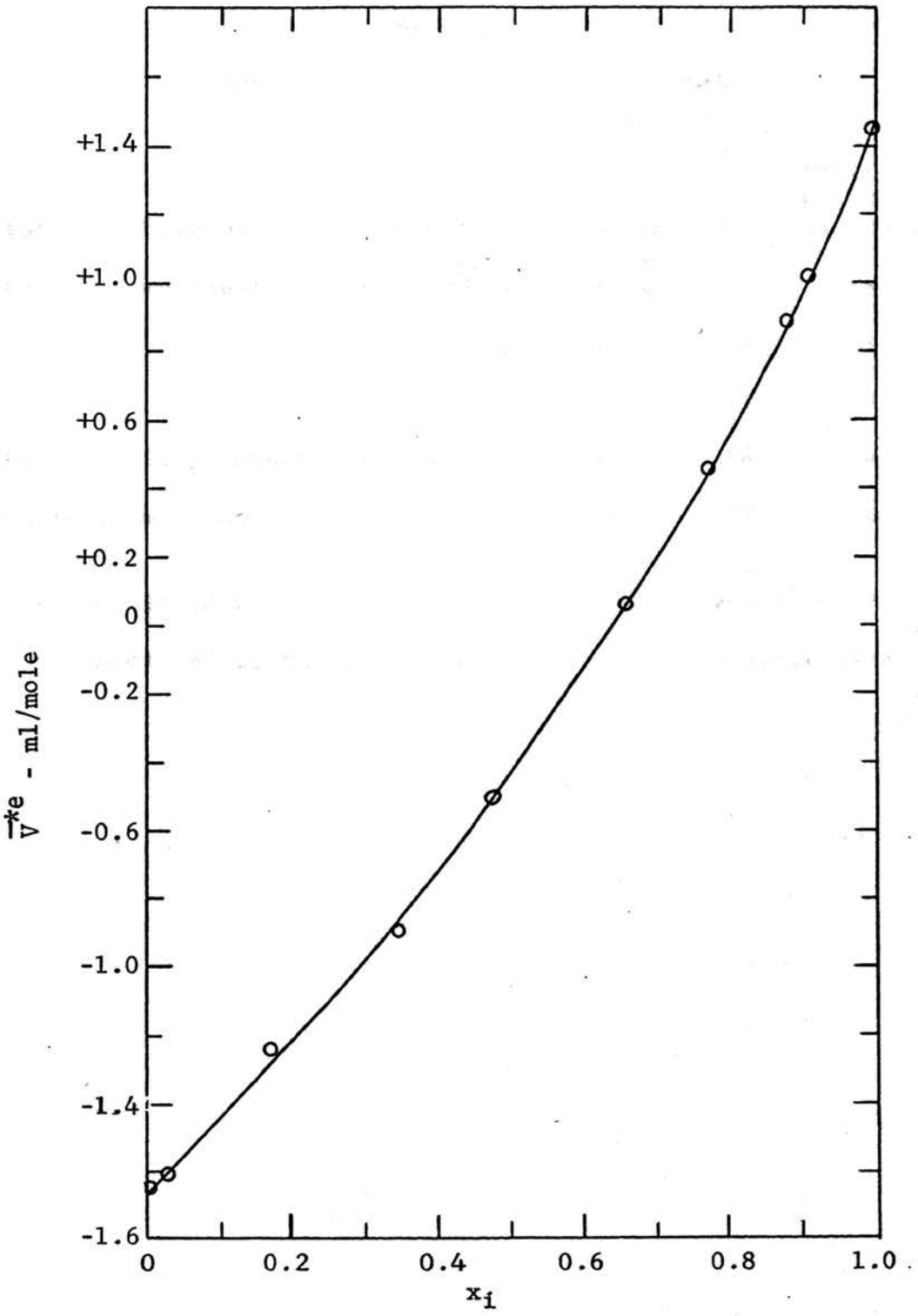


Figure 8A. Partial Molar Excess Volume of Acetone at Infinite Dilution.

TABLE IX

COMPARISON VALUES FOR PARTIAL MOLAR EXCESS VOLUMES AT INFINITE DILUTION

Solute	Solvent	This work	Literature	Ref.	Method used for obtaining literature value
water	methanol	-3.75 $\frac{ml}{mole}$	-3.88 $\frac{ml}{mole}$	23	a
			-3.62	24	a
			-3.48	25	a
water	isopropanol	-3.58	-3.42	26	a
n-butanol	methanol	0.57	0.58	27	b

a. Extrapolated to infinite dilution from pycnometric data.

b. Extrapolated to infinite dilution from dilatometric data.

The comparison values were obtained by extrapolation techniques from density data and have fairly large uncertainties associated with them, except where otherwise indicated. It is difficult to obtain very good precision in the density determinations of infinitely dilute solutions, consequently density measurements are not made at compositions very close to infinite dilution. The values presented here are probably the best available values of the apparent partial molar excess volumes for these solutes.

VI. Discussion of Results

The exothermic heat of mixing of methanol and isopropanol sets this system apart from systems of normal alcohols. The heats of mixing of 21 binary systems of normal alcohols have been reported.[12,13] The systems are made up of all the binary combinations of normal alcohols from methanol to decanol. The heat of mixing in all the systems studied is endothermic. In this investigation the heats of mixing of methanol and n-butanol with isopropanol have been determined and are exothermic.

The methanol-isopropanol system was chosen in part for the relatively small change in structuring with changes in the composition. However, a slight amount of structuring is indicated by the exothermic heat of mixing of -19.0 cal/mole. In comparison, the water-ethanol and water-methanol systems have exothermic minima in their heats of mixing of -186 cal/mole and -210 cal/mole respectively. It is evident that the majority of the previous measurements of heats of solution at infinite dilution in binary solvent systems were made in systems that exhibit substantially more structure than the methanol-isopropanol system. Since the change in free energy of mixing of the methanol-isopropanol system is not available, no attempts to explain heats of solution in this system in terms of structuring effects will be attempted. The heats of solution can be compared with the results of the investigation in other systems however. With the exception of argon, all other solutes in the water-ethanol and water-methanol system have been

observed to give an endothermic maxima in the heats of solution at infinite dilution.

If the components of a binary solvent system form an ideal solution, the heat of mixing of the components is zero, the heat of solution of a third component which does not form an ideal solution with either component should obey the relation

$$\Delta H_A^{sol'n} = x_1 \, \Delta\bar{H}_A^1 + x_2 \, \Delta\bar{H}_A^2 \qquad (35)$$

In equation (35) $\Delta\bar{H}_A^1$ and $\Delta\bar{H}_A^2$ are the heat of solution at infinite dilution of solute A in solvents 1 and 2, respectively. x_1 and x_2 are the mole fractions of the solvent components. The line connecting the heats of solution at infinite dilution in the pure components over the solvent composition range can be obtained from equation (35) and will henceforth be referred to as the "ideal" heat of solution.

The deviation of the heats of solution in systems containing water from the ideal heat of solution is in a positive direction; the heat effect is more endothermic than the mole fraction average of the heats of solution in the pure solvents. In the methanol-isopropanol system, the values obtained in this investigation deviate in a negative direction; they are more exothermic than the mole fraction average of the heats of solution in the pure components. From the results given in figure 7, the heat of solution of chloroform goes through a minimum and clearly cannot be equated to any type of arithmetic average of the pure solvent values.

Arnett et al.[1] have proposed an explanation for the heats of solution which assumes that enthalpy is an indicator of structural change, and that the position and height of the endothermic maxima observed in the ethanol-water system is a function of the size of the solute molecule. Bertrand, Larson, and Hepler[3] also observed changes in position and height of endothermic maxima for solute molecules of differing sizes in the water-triethylamine system. While the proposed explanation is qualitatively correct for the systems containing water, it is impossible to extend it to the methanol-isopropanol systems.

The explanation proposed by Krestov[9] in terms of the solute molecule occupying holes in the solvent structure of the methanol-ethanol system does not explain the heat effects observed in the methanol-isopropanol system. The minimum observed in the heat of solution of calcium nitrate in the low concentration region of ethanol is explained in terms of the disruption of the methanol structure by the ethanol molecules. They have also reported a maximum in the heat of solution in the region of low methanol concentration. The maximum is attributed to an enchancement of the stability of the ethanol structure since the molecules of methanol fit into the holes in the ethanol structure. The application of this interpretation to methanol-isopropanol predicts an endothermic maximum in the heat of solution of the solute in the region of low methanol concentration. For all of the solutes studied in this work, no endothermic maximum is observed; on the contrary, the heat observed is more exothermic than would be

expected from their explanation. In applying their explanation to the region of low isopropanol concentration, the effect due to size should be enchanced in this system due to the size of isopropanol relative to ethanol. None of the solutes studied in this investigation exhibit a minimum in the region of low concentration of isopropanol. The effects that Krestov observed apparently do not occur for non-electrolytes and must be assumed to be related to ionization of the solute.

Scatchard theory, as applied to three component systems with one component very dilute, indicates that the heat of solution should obey the equation,

$$\Delta H_A^{sol'n} = P_A H'_A + P_B H'_B - a\,\Delta H_{1\,2}^{mix} \quad . \tag{36}$$

P_A and P_B are either mole fractions or volume fractions of the solvent and a is a positive constant dependent on the solute. This equation can not predict heats of solution that deviate negatively from the "ideal" heat of solution for a solvent with a negative heat of mixing. Appendix I gives the derivation of an equation (A-8) that can be applied to heats of solution that show either positive or negative deviations.[28] The equation is in terms of the energy change on solution at constant volume.

$$\Delta E_A = v_1 \Delta E'_A + v_2\,\Delta E_A^2 - \bar{V}_A \left[\frac{\Delta E_{1,2}^{mix}}{V} + (2C_{A1}^{o} - 2C_{A2}^{o})(P_1 - V_1) \right] \tag{A8}$$

Lower case v's are volume fractions and ΔE_A^1 and ΔE_A^2 are the changes in energy of solute A dissolving in the pure solvents.

$\bar{V}_A$ is the molar volume of pure A, $\bar{V}$ is the molar volume of the solvent. The term $(2C^o_{A1} - 2C^o_{A2})$ is a solute-dependent parameter of the solvent system and P_1 is a weighted volume fraction, as explained in Appendix I. Substituting the relation given in Appendix I for P_1

$$P_1 = \frac{Bv_1}{Bv_1 + v_2} \quad , \tag{A10}$$

into equation A8 and rearranging terms,

$$\Delta(\Delta E) = \Delta E_A - v_1 \Delta E^1_A - v_2 \Delta E^2_A + \frac{\bar{V}_A}{\bar{V}}(\Delta E^{mix}_{1,2}) = (2C^o_{A1} - 2C^o_{A2}) \frac{v_1 v_2 (B-1)}{(B-1)v_1 + 1} \quad . \tag{37}$$

The term on the left of equation (37) can be evaluated from the data obtained in this investigation. Dividing equation (37) by $(v_1 v_2)$ and inverting

$$\frac{v_1 v_2}{\Delta(\Delta E)} = \frac{v1}{\bar{V}_A(2C^o_{A1} - 2C^o_{A2})} + \frac{1}{\bar{V}_A(2C^o_{A1} - 2C^o_{A2})(B-1)} \quad . \tag{38}$$

Equation (38) is a linear form from which the parameters $(2C^o_{A1} - 2C^o_{A2})$ and B can be evaluated.

Heats of solution are measured at constant pressure and must be converted to the energy at constant volume. They were converted

$$\Delta E_v = \Delta H_p - T \frac{\alpha}{\beta} \phi \bar{V}^e \tag{39}$$

by use of the equation (39). In this relation, α and β are the coefficients of thermal expansion and isothermal compressibility, respectively, of the solvent. α and β were approximated from values of the pure components by the following relationships, which are

valid for a solvent system which has no excess volume.

$$\alpha = v_1 \alpha_1 + v_2 \alpha_2$$
$$\beta = v_1 \beta_1 + v_2 \beta_2 \qquad (40)$$

Values for α were determined experimentally for the pure components ($\alpha_{meOH} = 11.8 \times 10^{-4}$ deg^{-1}, $\alpha_{iPrOH} = 10.4 \times 10^{-4}$ deg^{-1}) and for the equal volume mixture ($\alpha_{mix} = 11.0 \times 10^{-4}$ deg^{-1}). The experimental value obtained for the mixture was within one per cent of the calculated value.

Since the change in volume on mixing of methanol and isopropanol is small, about 0.03 ml/mole, the heat of mixing at constant pressure is approximately equal to the change in energy of mixing at constant volume. The values obtained for the parameters by calculation are presented in table X. Since in some cases it is impossible to obtain experimental values for the apparent partial molar excess volume and would be impossible to convert the heat of solution at constant pressure to the energy of solution at constant volume, the ΔE's in equation A-8 have been replaced by ΔH to give equation (41).

$$\Delta H_A = v_1 \Delta H_A^1 + v_2 \Delta H_A^2 - \bar{V}_A \left[\frac{\Delta \bar{H}_{1,2}^{mix}}{\bar{V}} + (2C_{A1}^o - 2C_{A2}^o)' (P_1' - v_1) \right] \qquad (41)$$

By a treatment similar to that given equation A-8, equation (41) can be converted to a linear form. The values of the parameter $(2C_{A1}^o - 2C_{A2}^o)'$ and B' have been evaluated for this equation and are presented in table X also.

The value of $(C_{11}-C_{22})$ has been calculated from equation A-9.

$$(C_{11}-C_{22}) = 2\ (C^{o}_{A1}-C^{o}_{A2}) + \frac{(\Delta E^{1}_{A}-\Delta E^{2}_{A})}{\overline{V}_{A}} \qquad (42)$$

This quantity should have a constant value since it is a function of the energy of interaction of pure solvent components. There is considerable variation in the value obtained, however.

The variations in shapes of the heat of solution curves in this "simple" system show that there are considerable solvent effects. Although these effects are smaller in magnitude than those in the water-ethanol system they are not amenable to simple explanations.

TABLE X

VALUES OF PARAMETERS
(from Equation 38)

Parameter	Water	Solute Acetone	n-Butanol	Chloroform
B	0.350	0.52	1.0	0.20
$2(C^{o}_{A1}-C^{o}_{A2})(\frac{cal}{ml})$	82.6 $\frac{cal}{ml}$	.21 $\frac{cal}{ml}$	undefined	11.7 $\frac{cal}{ml}$
$\bar{\delta}$ (cal)	$\pm$3	$\pm$1.5	$\pm$1	$\pm$6.0
δ_{max} (cal)	13	3	2	14
$(C_{11}-C_{22})(\frac{cal}{ml})$	-23.4	-5.7	--	-6.6

(from equation 41)

Parameter	Water	Acetone	n-Butanol	Chloroform
B'	0.33	.46	0.29	.18
$2(C^{o}_{A1}-C^{o}_{A2})'(\frac{cal}{ml})$	88.8	21.9	.32	11.0
$\bar{\delta}$ (cal)	$\pm$3	$\pm$2	$\pm$1.5	+7
δ_{max} (cal)	11	3	9	15
$(C_{11}-C_{22})'(\frac{cal}{ml})$	-28.3	-3.6	-3.0	-7.2

$\bar{\delta}$ is the average deviation of the calculated energies and energies of solution from the smoothed values obtained from the curves.

δ is the maximum deviation of the calculated heats and heats of solution from the smoothed values.

VII. Summary and Recommendations

In this investigation the heats of solution at infinite dilution and the partial molar excess volume of four solutes have been determined in the methanol-isopropanol solvent system, and the measured values are shown to correspond to the defined thermodynamic functions. The results of this investigation have been presented along with the relative partial molar enthalpies and the heat of mixing curve of methanol and isopropanol. The values of the heats of solution and the apparent partial molar enthalpies were compared where possible with literature values.

The values were compared with the explanations for the heats of solution in ethanol-water and methanol-ethanol solvent systems. The explanations presented for those systems were found to be inadequate to explain the results in the methanol-isopropanol system.

The relative partial molar enthalpies of two different normal alcohols were found to be negative in isopropanol while they are always positive in normal alcohol systems. The heats of solution of normaland branched alcohols have not been studied extensively.

The apparent partial molar excess volumes of the solutes were determined and these values utilized to convert the heat of solution at constant pressure to the energies of solution at constant volume. The energy changes were used to compute the values of the parameters in an equation for the energy of solution derived by G.L. Bertrand[28] and presented in Appendix I.

It is felt that a continuation of this study in terms of more

solutes in this system and also extending to other systems will provide data on the effects of the solutes and insight into the energies of interaction of the solvents so that the solvent effects may be better understood and explained.

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Appendix I

HEATS OF SOLUTION IN BINARY SOLVENT SYSTEMS

The major problems involved in attempts to develop theories and equations pertaining to the heats of mixing of liquid mixtures are: description of the average environment of a given molecule, estimation of the total number of interactions in which that molecule is involved, and description of the average energy of the molecule in terms of its interactions with its environment. The different equations that have been derived for heats of mixing differ only in the model chosen for the three effects listed above. In the case of a binary system with one component very dilute (approaching infinite dilution) all of the equations yield a relationship similar to the one which Scatchard [1] derived:

(1) $\Delta\bar{E}_A = -\bar{V}_A(2C_{AS}-C_{AA}-C_{SS})$

$\Delta\bar{E}_A$ Partial molar excess energy of the solute, A, at infinite dilution in solvent, S.

$\bar{V}_A$ Molar volume of pure solute

C_{ij} Average absolute value of the energy of interaction between the solute and the solvent (per unit volume).

This equation is independent of the model chosen to describe the environment of a solute molecule, since only solute molecules surround the solute at infinite dilution. To apply this equation to a binary solvent system (components 1 and 2), a model must be chosen to describe the parameters C_{AS} and C_{SS} in terms of the solvent composition (X_1). Both Scatchard[1] and Hildebrand[2] have

chosen an approximation

(2) $C_{ii} = + \Delta E_i^{vap} / \bar{V}_i$

for the energy of the interactions within a pure solvent. Applying this approximation to a mixed solvent (assuming no excess volume) we obtain

(3) $C_{SS} = \Delta E_S^{VAP} / (X_1 \bar{V}_1 + X_2 \bar{V}_2) = v_1 C_{11} + v_2 C_{22} - \Delta E_{12}^{mix} / \bar{V}$,

where the lower case v's represent volume fractions and the upper case $\bar{V}$ represents the molar volume of the mixture.

There is no precedent in the literature for a model on which to base approximations for C_{AS} in terms of solvent composition. This term can be described with the equation

(4) $C_{AS} = p_1 C'_{A1} + p_2 C'_{A2}$,

where p_i represents the probability that the solute will interact with a solvent molecule of type $\underline{i}$ and C'_{Ai} represents the energy of the interactions between the solute and that type of solvent in the environment that prevails at that particular solvent composition. As a first approximation, we choose

(5) $C'_{Ai} = C^o_{Ai}$,

independent of solvent composition. Substituting equations 3, 4, and 5 into 1, we obtain

(6) $\Delta \bar{E}_A = -\bar{V}_A (2p_1 C^o_{A1} + 2p_2 C^o_{A2} - C_{AA} - v_1 C_{11} - v_2 C_{22} + \Delta E_{12}^{mix} / \bar{V})$.

Solving equation 6 for the cases of the two pure solvents,

(7)
$$\Delta \bar{E}^1_A = -\bar{V}_A (2C^o_{A1} - C_{AA} - C_{11})$$
$$\Delta \bar{E}^2_A = -\bar{V}_A (2C^o_{A2} - C_{AA} - C_{22})$$

Combining equations 7 with 6, we obtain

$$(8)\quad \Delta \bar{E}_A = v_1 \Delta \bar{E}_A^1 + v_2 \Delta \bar{E}_A^2 - \bar{V}_A \left[\Delta E_{12}^{mix}/\bar{V} + (2C_{A1}^o - 2C_{A2}^o)(p_1 - v_1) \right] .$$

Equation 8 may be recognized as very similar to the equation that may be derived from the equation of Hildebrand[3] with two exceptions: this equation should apply equally well to positive and negative heats of solution and the final term of equation 8 does not appear in the Hildebrand equation. Two difficulties remain in equation 8; the terms C_{Ai}^o and the probability term, p_1. Equations 7 can be combined to yield the difference in the C_{Ai}^o values in terms of the $\Delta \bar{E}_A^i$ values and a parameter which is a property of the solvent system.

$$(9)\quad 2\ (C_{A1}^o - C_{A2}^o) = (C_{11} - C_{22}) - (\Delta \bar{E}_A^1 - \Delta \bar{E}_A^2)/\bar{V}_A$$

The simplest approximation for the probability term is to assume that it can be represented as a weighted volume fraction:

$$(10)\quad p_1 = Bv_1/(Bv_1 + v_2).$$

This allows the representation of data by a two parameter equation. The validity of the approximations and assumptions of this treatment will depend on whether the parameter $(C_{A1}^o - C_{A2}^o)$ for several solutes in a single solvent system can be reduced to a single parameter through equation 9.

In applying this equation one must be aware of the types of systems in which the approximations may be expected to be valid. At the present time it is felt that the only systems to which this treatment might apply are those in which the solvent components are very similar, such as mixtures of two alcohols, two hydrocarbons, etc.

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